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Possible Evidence for Life in ALH84001; David McKay¹, Everett Gibson¹, and Kathie Thomas-Kep²; ¹NASA/Johnson Space Center, SN, Houston, TX 77058, ²Lockheed-Martin, C-23, Houston, TX 77058

Since our original paper in Science in August 1996 [1], considerable new data has appeared from laboratories throughout the world, and our own team has had a chance to examine the sample in greater detail. The following summary touches on our original data and interpretation, and points out new data from us and from other groups, and the resulting changes and refinements in interpretations which we have made during the past three years.

Polycyclic aromatic hydrocarbons (PAHs) in the meteorite

We found organic compounds- polycyclic aromatic hydrocarbons (PAHs) within the meteorite and proposed that they were indigenous and came from Mars. We proposed that they may represent products from the decay of once-living martian organisms. We did not analyze for other organics such as amino acids. Members of our team have now completely reanalyzed the meteorite for PAHs and have also analyzed the Allan Hills ice and micrometeorites collected in Antarctic ice fields [2]. The conclusion [2] is that Allan Hills does indeed have indigenous PAHs from Mars, they did not come from the Antarctic ice, and the variety of PAHs and abundance patterns in Antarctic micrometeorites is diverse and not like those in ALH84001. This paper concludes that contamination with PAHs of porous samples by Antarctic melt water or wind-blown dust is not a universal process and may not exist at all. Other conclusions are that the Allan Hills ice does not contain detectable PAHs at levels a thousand times below the levels measured in ALH84001, and there is no verifiable laboratory evidence that carbonates can concentrate PAHs from solution. Taken together, these data make it difficult to suppose that PAHs in ALH84001 are the result of contamination from melt water. Furthermore, the increase in PAH abundance from the fusion crust (actually from the heated portion of the meteorite slightly inside of the fusion crust) to the center has been verified for all traverses, again supporting an indigenous origin for the PAHs.

The PAH distribution was described by Stephan and co-workers using TOF-SIMS (time-of-flight secondary ion mass spectrometry) analysis of polished thin sections seemed to show that PAHs were not associated with carbonates and were highest in the pyroxenes [3]. These data are difficult to reconcile with the detailed data of the Clemett group. We suggest that the thin section making technique may have created artifacts from the material used in the section production process (organic solvents and diamond paste), or from the smearing of existing PAHs over the polished surfaces. A close comparison of the TOF SIMS technique used by [3] to the laser ablation technique used by [2] has not been made, even for standards. Therefore it is difficult to compare the two sets of data even if they were analyzing the same thing which they are not. Until the TOF-SIMS group [3] analyzes the natural fractures surfaces in the meteorite and also shows that they can detect equivalent PAHs in comparison standards also analyzed by the laser ablation technique [2], their data must be treated very cautiously. Contrary to the results of [3], small areas containing high concentrations of organics have been documented within the carbonate globules within TEM thin sections [4]. It is very difficult to imagine how these organic carbon compounds within the interior of the martian carbonates could have been formed on Earth.

Our own group has detected evidence of recently growing terrestrial bacteria (identified tentatively as *Actinomyces*) in ALH84001 located on surfaces near the fusion crust [5]. It seems likely that this bacteria grew in Antarctica. It is rare and patchy and we have found it in abundance on only one chip. It is possible that decay of these bacteria and their appendages could form PAHs. However, the documented distribution of PAHs (highest in the interior and lowest near or at the fusion crust) argues against this explanation, as we have not found *Actinomyces* on fractures in interior chips, and have not detected it at all on most chips, including those with measured high levels of PAHs. The amino acids reported by Bada and coworkers [6] in ALH84001 may indeed be mostly or entirely terrestrial; amino acids are much more soluble in melt water than PAHs and are there likely to move

around and to be deposited in meteorites. The amino acids could also be partially derived from the *Actinomyces*. The addition of Antarctic organic compounds to ALH84001 in no way proves that martian ones are not there; it simply makes their identification more difficult.

The work by Jull and coworkers showed that much of the organic content in ALH84001 is indeed terrestrial contamination, but they also found that 10-20% of the carbon was not terrestrial (no carbon-14) and also had a light or negative (-18) carbon isotope ratio making it unlike the carbon in the martian carbonates analyzed by ion microprobe [7]. A straightforward but not exclusive interpretation is that this material is organic carbon which came from Mars. It may or may not include the PAHs identified by our team.

In summary, we believe the evidence is stronger than ever that some organic compounds from Mars are found in this meteorite. However, most (80%) of the organic compounds in the meteorite may come from Antarctica. Our original interpretation that the PAHs may be products from fossil decay on Mars remains unchanged. None of the new data bring us any closer to resolving whether these martian organic compounds actually come from living systems or from non-biologic sources on Mars. We conclude that the PAHs are potential biomarkers for this meteorite, that some of the PAHs are indigenous to the meteorite and therefore from Mars. However, as with our original paper, the presence of indigenous martian PAHs is not sufficient evidence for martian life, but it is certainly compatible with that explanation.

The carbonates as biologically assisted minerals

We originally proposed that the carbonate globules or pancakes may have been formed with the assistance of microbes. Many terrestrial examples exist of small carbonate nodules formed with the help of bacteria or algae. If microbes assisted in the formation of the carbonates, then the carbonates presumably formed at temperatures where life could exist. From earth examples, this temperature could not exceed about 115°C. If the carbonates formed at higher temperatures, microbial assistance is unlikely. Debate still rages over the temperature of formation of these carbonates, but a consensus seems to be developing that low temperatures are a more likely environment for their formation [e.g., 8]. A low temperature formation as a precipitation from a water-bearing fluid would allow for microbial assistance but does not require it. The presence of mica (layer lattice silicates) [9] within and touching the carbonates suggests that liquid water was indeed present and that the carbonates formed at low temperatures. The presence of organic carbon within the carbonates also suggests low temperatures and possibly microbial participation, although non-biologic organic carbon may have been incorporated. No unequivocal evidence for microbes within carbonates has been identified. However, these carbonates have been modified by shock effects and subsequent heating in some cases. Our original hypothesis that these carbonates were biologically assisted during their formation remains unproven, but has not been disproved and therefore is still viable. An additional hypothesis has arisen in which the carbonates accumulated detrital grains of bacteria fragments and small oxides, sulfides, and other material during carbonate growth [10]. In this hypothesis, the carbonates were not influenced by microbes, but may have passively accumulated their remains. Some evidence supporting this detrital hypothesis exists (see magnetites). This hypothesis relaxes considerably the temperature constraints for the inclusion of biogenic products such as microbe parts or biominerals. Another possible complexity is that the iron- and sulfur-rich rims may have formed at a temperature different from the main body of the carbonates. Little evidence is available to answer this question. The formation in various earth environments of complexly zoned, highly non-equilibrium carbonate globules or concretions is not well understood, and unequivocal means to tell biological carbonates from non-biological ones are not well developed. Consequently, the presence, the chemistry, and the texture of the carbonates at this point neither supports nor contradicts the hypothesis that they have been formed with the assistance of microbes. Recently it was discovered that the Tatahouine meteorite contains carbonate pancakes and tiny forms interpreted as bacteria, all of which formed in the Liberian desert at ambient temperatures [11].

Possible biominerals: the magnetites

We originally found tiny (10-100 nanometer) crystals of iron sulfide and iron oxide within the carbonates. We suggested that the magnetites may have been formed by bacteria because they were similar to known magnetites formed by magnetotactic bacteria on earth. We pointed out that some earth bacteria also form tiny iron sulfide minerals.

Results of a complete restudy of the magnetites is given in this volume [12]. Our new conclusion is that a subpopulation of magnetites exists in the rims of the carbonates and the properties of this subpopulation can only be produced by magnetotactic bacteria. Other magnetites may or may not be biogenic. All could form at low temperatures including the whiskers. A detrital origin of many magnetites in the carbonates cannot be ruled out. The ground water from which the carbonates precipitated could have contained abundant suspended magnetites of various origins which became trapped in the growing carbonates. The iron-rich rims could have formed during a period when suspended magnetites were abundant in the ground water. Ground water containing magnetites including likely biogenic magnetites is found in terrestrial environments [10]. Intermixed biologic and non-biologic magnetites are common in many earth sediments [e.g., 13].

The magnetites of ALH84001 consist of several distinct types. Some of these magnetites, mainly the whiskers with central screw dislocations, are known only from non-biologic environments. Other types of magnetite including the various irregular forms which comprise more than two-thirds of the martian magnetite may be from either microbial sources or totally non-biologic sources; these magnetites are not distinctive enough to allow us to tell the difference. However, one type has very distinctive properties known on earth only from microbial production. This type comprises more than a quarter of all the martian magnetites in this meteorite. If found on earth, such magnetites would be considered by most magnetite experts to be absolute proof of biologic activity. Unless future work identifies this distinctive form of magnetite in other kinds of environments on earth, their presence in martian meteorite ALH84001 can be taken as very strong evidence in support of our original hypothesis that this meteorite contains evidence for early life on Mars; some would call this the smoking gun. The coexistence in ALH84001 carbonates of this distinctive biogenic magnetite with other types which may be non-biogenic is an additional complication which is simply not well understood, but it may be analogous to the presence of intermixed biologic and non-biologic magnetite in many earth sediments.

The sulfides as biominerals.

We originally found two types of iron sulfide in the rims of the carbonates which we identified as pyrrhotite and an iron monosulfide, tentatively identified as greigite. We proposed, based on terrestrial examples, that they might also be biominerals formed by microbes. While the sample contains pyrite, another form of iron sulfide, we did not find any in the rims of the carbonates. No one has yet determined the isotopic composition of the tiny sulfides in the carbonates; existing analyses are either much larger sulfides or are bulk sulfur isotopes in the region of the carbonates.

Not much new has been discovered about the sulfides. We have confirmed that pyrrhotite (FeS_2) is indeed present in the rims of the carbonate globules. Others have measured the isotopic composition of the pyrites and have found no significant fractionation which could be caused by biogenic activity. However, on earth sulfides produced by bacterial activity sometimes do not show any kind of fractionation of sulfide isotopes; the significance of iron sulfides as a biomineral remains problematical. No one has yet accurately measured the isotopic composition of the tiny (10s of nanometer in size) iron sulfides in the rims. The issue of whether these tiny rim sulfides could be formed or assisted by microbes remains open. No data currently exist which either prove or disprove this hypothesis. It is not critical to our overall story, particularly if the rims contain detrital minerals trapped from ground water.

Fossil-like forms

Subsequent examination by our group and others has confirmed that a diverse variety of features exist on the surfaces of the carbonates and even on the pyroxene surfaces. Sizes of these features range from a few tens of nanometers to more than a micrometer in longest dimension. It has

been argued that some or all of these features are artifacts of coating, artifacts from the edges of larger crystal structures, or weathering products introduced into the sample in Antarctica. The existence of very small bacteria remains controversial. The work by Kajander and his co-workers [14] has shown that viable microbes can exist at sizes down to about 100 nanometers, but below this size units do not appear to be viable, and may be fragments of larger units. The size of these features is compatible with some of those we described in ALH84001. The effect of extreme stress, for example total drying out, on microbes is not well understood, but is known to include significant reduction in size. Whether this reduction could form viable units smaller than 100 nanometers remains to be seen. Larger spherical or elongated features in ALH84001 (and other martian meteorites) nanometers in size cannot be excluded as possible martian microfossils on the basis of size alone; other criteria are necessary and we [15] and others are actively working on developing such criteria. We agree with Bradley and co-workers that some of the features we have shown in the press photos and talks are likely to be artifacts of a combination of crystal faces from carbonates, pyroxenes, and clay minerals along with a thickening of features resulting from the application of a conductive coating. In general, this artifact interpretation applies to long thin worm-like forms which appear to be parallel. We have now proposed that some of the elongated features in ALH84001 are neither intact fossil microbes or artifacts, but may be fragments or parts (flagella, filaments, etc.) of larger bacteria [16]. Such fragment remains are common in the fossilized remains of some earth bacteria. Filaments may be as thin as 5 nanometers and may have lengths up to a micrometer or more. A good example is a long filament found in ALH84001 and illustrated in [16]. A combination of morphology, chemistry, and mineralogy is necessary to characterize such fragments.

Small rounded, ovoid, and wormy features can form by totally non-biologic processes and have now been documented in calcite precipitation [17]. Other small features which mimic the appearance of microbes may in fact be clay minerals of various types. Some amorphous silica is known to form initially as tiny spheres. The broad topic of the shapes and sizes of nanometer-sized inorganic colloids, amorphous gels, and crystal nuclei is only poorly understood, partly because the proper tools have not been available until recently. We discuss criteria for separating such inorganic features from true fossils in this volume [15]. It is clear that great caution must be taken in interpreting the presence of such nanometer-sized features in both terrestrial and extraterrestrial samples.

Summary

We know of no single inorganic explanation which can explain the chemistry and textures of the carbonates extreme zoning of mineralogy, bulk chemistry, and isotopes, the presence of PAHs within the carbonates, on the surface of fractures, and depleted at the fusion crust, the presence of diverse populations of magnetite (including ones identical to the unique biogenic forms on earth) within the carbonates, and the presence of fossil-like mineralized forms within and on fracture surfaces and on the surface of the carbonates.

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